Electric Field-Induced Piezoelectricity in Polymer Film

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Synopsis

An apparatus is devised for measuring the real and imaginary components of the piezoelectric strain constant $d = d' - id''$ for polymer films with a d.c. bias field. Electric field-induced piezoelectricity is observed for films of several types of polymer. The ratio of the piezoelectric constant to the d.c. bias field gives $(\epsilon + \kappa)/G$, where ϵ is the dielectric constant, κ is the electrostriction constant, and G is the elastic constant. The temperature dependence of the field-induced piezoelectricity gives, therefore, combined information of dielectric and elastic properties of polymers. After heating to about 95°C followed by cooling to room temperature, maintaining a constant d.c. bias on a poly(vinyl chloride) film, piezoelectricity is observed at null d.c. field, which suggests the introduction of a residual polarization in the film.

INTRODUCTION

Piezoelectricity in electretized polymer films has aroused much interest for the last several years.[1-6] A variety of polymer films can be transformed into electret by applying a high electric field at high temperature and cooling under the field. Such electret polymers often show a large piezoelectric effect. A study has also been reported on the piezoelectric effect in polyethylene films with a d.c. bias field.[7] It has been suggested that this type of piezoelectricity is caused by the coupling effect of electrostriction and the induced polarization.[8] This paper will present observations on electrically induced piezoelectricity in some polymer films.

EXPERIMENTAL

Piezoelectric strain constant d is defined as the polarization P produced by a unit magnitude of stress T at a condition under which the measuring electric field E across the film is zero:[9]

$$d = \left(\frac{\partial P}{\partial T}\right)_{E=0}$$

In polymers, d is a complex quantity and expressed as $d = d' - id''$.[10] We have devised an apparatus by which both d' and d'' are determined for polymer films with a d.c. polarizing field. The frequency chosen was 20 Hz, and the tempera-

ture of the sample was varied from $-150°C$ to $+100°C$. The size of sample was roughly $50 \times 8 \times 0.05$ mm, and aluminum was vacuum deposited on both surfaces as electrodes.

Figure 1 shows a schematic diagram of the apparatus. A sinusoidal oscillation is given to the film longitudinally at 20 Hz by an electromagnetic driver. The current in the driving coil indicates the magnitude of the stress in the sample. In order to cancel out the piezoelectric voltage across the film, a canceling voltage is derived from the driving current and supplied through capacity C (1000 pF) and resistance R (10 MΩ): the former cancels the component of the piezoelectric voltage in phase with the stress, and the latter cancels the component of the piezoelectric voltage $90°$ out of phase. The unbalanced voltage from the sample is amplified and led to phase-sensitive detectors, the reference voltage of which is either in phase or $90°$ out of phase with the driving current. By adjusting two potentiometers (1000 Ω, 10 turn), null indication in the output voltages from the phase-sensitive detectors is observed in a two-beam oscilloscope. The force applied sinusoidally was about 7.5 g weight, peak-to-peak; for a typical sample, the deformation was about 5 microns. At the null condition, the potentiometer readings give the values of d' and d'' as follows:

$$d' = \alpha \frac{tw}{A} C\theta'$$

$$d'' = \alpha \frac{tw}{A} \frac{1}{\omega R} \theta''$$

where t is the thickness, w is the width, A is the electrode area, ω is the angular frequency, θ' is the reading of the potentiometer connected to $C = 1000$ pF, θ'' is the reading of the potentiometer connected to $R = 10$ MΩ, and α is the force transducer constant $\alpha = 2.7$ volts/newton.

A d.c. electric field was applied to the film through a filter during measurements of the piezoelectric coefficients. By an electrometer connected in series with the sample, the polarization and depolarization currents are determined simultaneously with piezoelectric measurements.

RESULTS

Figure 2 shows the piezoelectric strain constant d' and d'' for several types of polymer films induced by applying a d.c. electric field. A good linearity was observed between the piezoelectric constants and the electric field. At an electric field of 10^6 volts/meter, the value of d' for nonelectretized poly(vinylidene fluoride) (PVF$_2$) is 7×10^{-14} coulomb/newton, which is small compared to the piezoelectric constant of crystals (for quartz $d = 2 \times 10^{-12}$ coulomb/newton), and small compared to the reported[1] piezoelectric coefficient $d' = 7 \times 10^{-12}$ coulomb/newton for the electret PVF$_2$.

Figure 3 shows similar relations between the d' and d'' constants and the electric field for a poly(vinyl chloride) film (PVC) at different temperatures. To avoid electretizing the film, the d.c. bias field was reversed in sign in successive measurements. A good linearity was observed for both d' and d'' at all observation temperatures.

Figure 4 illustrates the temperature dependence of d' and d'' for PVC under a constant d.c. bias field of 2×10^6 volts/meter. Both d' and d'' increased mark-
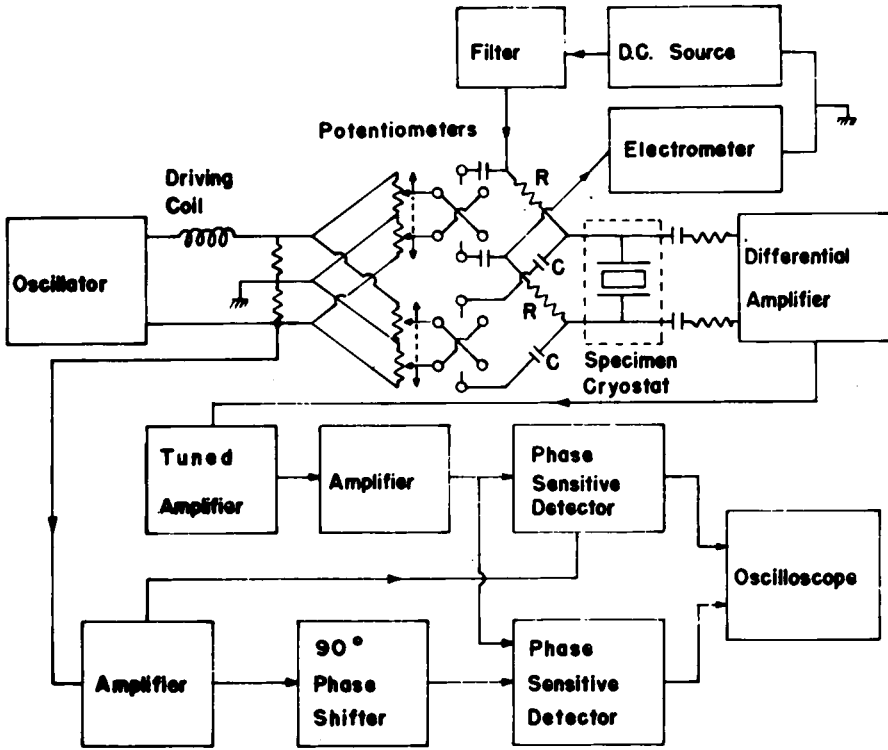
Fig. 1. Schematic diagram of the apparatus for measuring inherent and electric field-induced piezoelectricity. For a null indication on the oscilloscope, the two precision potentiometers read the real and imaginary components of the piezoelectric strain constant $d = d' - id''$. Simultaneously, the electrometer measures the field-induced conduction and polarization current, or measures the depolarization current with the d.c. source shorted to ground.
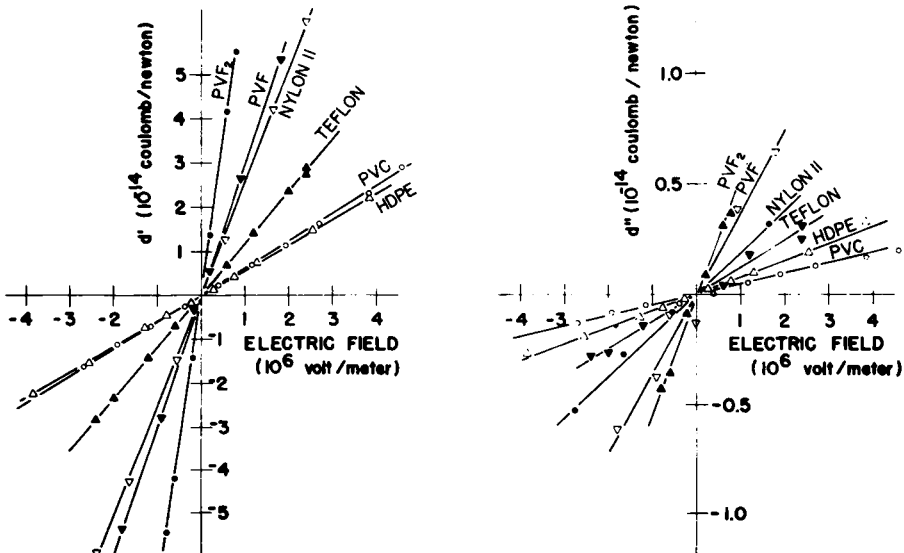
Fig. 2. The real and imaginary components of the piezoelectric strain constant $d = d' - id''$ for several types of polymer films induced by applying a d.c. bias field.
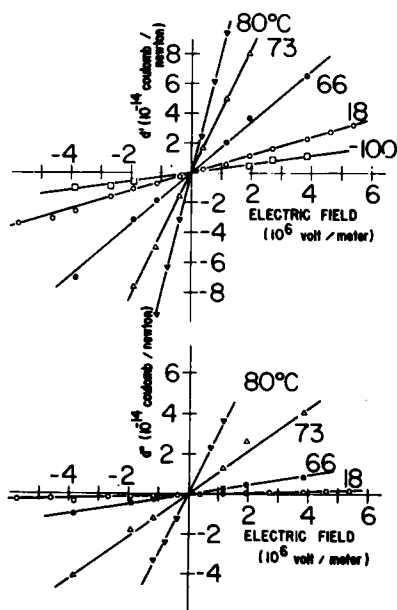
Fig. 3. The electric field-induced piezoelectric strain constant components $d = d' - id''$ for poly(vinyl chloride) film at several temperatures.
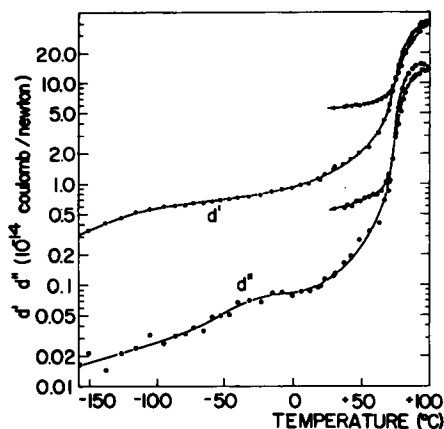

Fig. 4. The temperature dependence of the piezoelectric constants d' and d'' for poly(vinyl chloride) with a constant d.c. bias field of 2×10^6 volts/meter. The cooling curve differs markedly from the heating curve because the sample retains a permanent polarization when cooled under an applied electric field.

edly near the glass transition temperature (about 80°C). The d.c. conductivity determined simultaneously with the piezoelectric measurements also increases sharply at the same temperature.

Figure 5 shows the d.c. field dependence of d' and d'' measured at room temperature in the same PVC sample before and after heating. Curve a shows the data for the new sample before heating. It shows that the induced piezoelectricity is linearly related to the d.c. bias field. The straight line does not pass through the origin. This indicates that a slight residual polarization is already present in the sample. After decreasing the temperature from 95°C maintain-
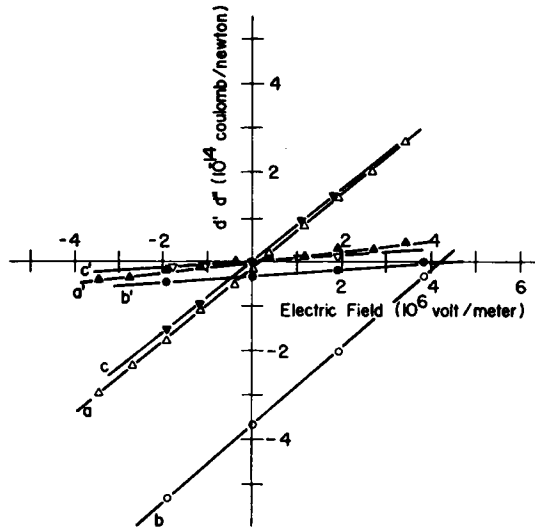
Fig. 5. Electric field-induced piezoelectric strain constants d' and d'' following heat treatment of a single poly(vinyl chloride) sample. Curves a and a′ demonstrate that the original sample contained a small residual polarization. Curves b and b′ show the polarization retained by the sample after cooling from 95°C with an applied electric field of -2×10^6 volts/meter. Curves c and c′ demonstrate the annealing effect of cooling the sample from 80°C with short-circuited electrodes. All three sets of measurements were made at constant temperature 20°C.

ing the d.c. field of 2×10^6 volts/meter, the field dependence of d' and d'' was tested at room temperature. The resulting curve b shows that considerable piezoelectricity was observed at null d.c. bias field; in other words, residual polarization is introduced to the sample. The sample was then short-circuited between electrodes of the two surfaces and annealed at 75°C overnight. Curve c indicates the results observed at room temperature after such annealing. The residual polarization disappeared and the sample became unpolarized. The curves a′, b′, and c′ show corresponding data for d''. The slope of curves b′ and c′ is a little smaller than that of a′, suggesting that the loss tangent for piezoelectricity constant, $\tan \delta_d$, becomes smaller due to annealing.

DISCUSSION

In the present experiment, a longitudinal vibration is given to the sample film which is subjected to a constant d.c. voltage V between two surfaces of area A. From another point of view, the variation of capacity induces the variation of electric charge. The change of the capacity C with the longitudinal strain S is given by

$$\frac{\partial C}{\partial S} = \frac{\partial}{\partial S}(\epsilon C_0) = \frac{\partial \epsilon}{\partial S}C_0 + \epsilon \frac{\partial C_0}{\partial S}$$

where C_0 is the capacity in vacuum of electrodes with the same dimensions as the sample and ϵ is the dielectric constant. Assuming two Poisson ratios σ_1 and σ_2,

$$\frac{\partial C_0}{\partial S} = C_0(1 + \sigma_1 - \sigma_2).$$

Since $\sigma_1 \simeq \sigma_2$, we have

$$\frac{\partial C}{\partial S} = C_0(\kappa + \epsilon)$$

where $\kappa = \partial\epsilon/\partial S$ is the electrostriction constant.[11,8] Then the piezoelectric stress constant e is given by

$$e = \frac{\partial P}{\partial S} = \frac{1}{A}\frac{\partial}{\partial S}(CV) = \frac{V}{A}C_0(\kappa + \epsilon) = E_0(\kappa + \epsilon)$$

and the piezoelectric strain constant d is expressed as

$$d = e/G = E_0\frac{\kappa + \epsilon}{G}$$

where G is the elastic constant and E_0 is the d.c. bias field.

The slope of the lines between d and E_0 as shown in Figures 2 through 5 indicates, therefore, the values of $(\kappa + \epsilon)/G$, a quantity involving the electrostriction constant κ, the dielectric constant ϵ, and the elastic constant G.

Figure 2 indicates that the value of d'/E_0 for various kinds of polymers is of the order of 10^{-20} meter^2/volt^2.

If we assume typical values for κ, ϵ, and G, we have $\kappa + \epsilon = 3 \times 10^{-11}$ farad/meter, and $G = 3 \times 10^9$ newtons/meter^2, and $(\kappa + \epsilon)/G$ becomes 10^{-20} farad-meter/newton, the same order as the observed values.

The present method of measuring the field-induced piezoelectricity gives, therefore, a combined information of dielectric and elastic properties of polymers. If the electrostriction constant κ is ignored, the apparent piezoelectric constant determines the ratio of ϵ to G or the product of ϵ and the compliance $(1/G)$. Since both ϵ and G are relaxational quantities of polymers, d should also be a relaxational quantity.

The increase of d' and d'' at the higher temperature as shown in Figure 4 can be ascribed to the increase of ϵ and the decrease of G.

The piezoelectric loss tangent, $\tan \delta_d$, is expected to be the sum of the dielectric loss tangent $\tan \delta_\epsilon$ and the elastic loss tangent δ_G.[12] From the data in Figures 2 and 3 we have the value of $\tan \delta_d = d''/d'$ in the order of 10^{-1}. Since the order of $\tan \delta_\epsilon$ and δ_G is 10^{-2}, the observed value of $\tan \delta_d$ should be the sum of these two.

As illustrated in Figure 2, the field-induced piezoelectricity can be observed for any polymer with sufficiently high insulating resistance. It is noted that the apparent piezoelectricity is larger in polar polymers such as PVF$_2$ and PVC than in nonpolar polymers such as Teflon and polyethylene. When residual polarization is introduced by a prolonged polarization process as for PVF$_2$, much larger piezoelectricity is given to the sample, which persists even after removing the d.c. field.

It is hoped that the experiments described in this paper will be useful for understanding the basic properties of electret polymers and that field induced piezoelectricity affords combined information of dielectric and elastic properties of polymers and therefore a new physical parameter to indicate the relaxational properties of polymers.

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